

Kokai (Jpn. Unexamined Patent Publication) No. 5-98168

Title of the Invention: Aqueous Curable Resin Composition

Publication Date: April 20, 1993

Patent Application No. 3-259181

Filing Date: October 7, 1991

Priority Claimed: None

Applicant: Dainippon Ink & Chemicals, Inc.

Inventors: Masataka Oooka; Goro Iwamura; Shoichiro Takezawa

CLAIMS

1. An aqueous curable resin composition containing, as indispensable ingredients, an aqueous dispersion or an aqueous solution of a polymer (A) which contains, in each molecule, both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, and an aqueous dispersion or an aqueous solution of a polymer(B) which contains no 1,3-dioxolan-2-one group.

2. An aqueous curable resin composition containing, as indispensable ingredients, an aqueous dispersion or an aqueous solution of a polymer (A) which contains, in each molecule, both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, and a curing agent (C), which is capable of reacting with a hydroxyl group.

3. An aqueous curable resin composition containing, as indispensable ingredients, an aqueous dispersion or an aqueous solution of a polymer (A) which contains, in each molecule, both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, an aqueous dispersion or an aqueous solution of a polymer (B) which contains no 1,3-dioxolan-2-one group, and a curing agent (C), which is capable of reacting with a hydroxyl group.

4. An aqueous curable resin composition containing, as indispensable ingredients, an aqueous dispersion or an aqueous solution of a polymer (A) which contains, in each molecule, both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, an aqueous dispersion or an aqueous solution of a polymer (B) which contains no 1,3-dioxolan-2-one group, and a curing catalyst (D).

5. An aqueous curable resin composition containing, as indispensable ingredients, an aqueous dispersion or an aqueous solution of a polymer (A) which contains, in each molecule, both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, a curing agent (C), which is capable of reacting with a hydroxyl group, and a curing catalyst (D).

6. An aqueous curable resin composition containing, as indispensable ingredients, an aqueous dispersion or an aqueous solution of a polymer (A) which contains, in each molecule, both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, an aqueous dispersion or an aqueous solution of a polymer (B) which contains no 1,3-dioxolan-2-one group, a curing agent (C), which is capable of reacting with a hydroxyl group, and a curing catalyst (D).

7. An aqueous curable resin composition according to any one of claims 1 through 6, wherein said polymer (A) is at least one resin selected from the group consisting of a vinyl polymer, a polyester resin, an alkyd resin, a polyurethane resin and a polyether resin.

8. An aqueous curable resin composition according to claim 7, wherein said polymer (A) is an acrylic polymer.

9. An aqueous curable resin composition according to claim 7, wherein said polymer (A) is fluoroolefin polymer.

10. An aqueous curable resin composition according to any one of claims 1 through 6, wherein said polymer (A) is one that has a hydroxyl group.

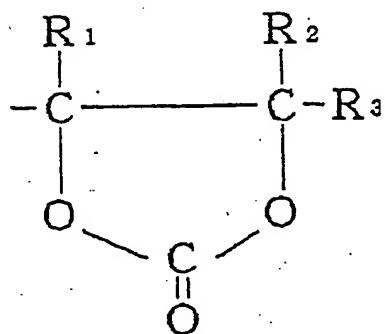
11. An aqueous curable resin composition according to any one of claims 1 through 6, wherein said polymer (B) is at least one resin selected from the group consisting of a vinyl polymer, a polyester resin, an alkyd resin, a polyurethane resin and a polyether resin.

12. An aqueous curable resin composition according to claim 1,3,4 or 6, wherein said polymer (B) has at least one group selected from the group consisting of a carboxyl group, a carboxylate group and a hydroxyl group.

13. An aqueous curable resin composition according to claim 2,3,5 or 6, wherein said curing agent (C) is an amino resin and/or a block isocyanate.

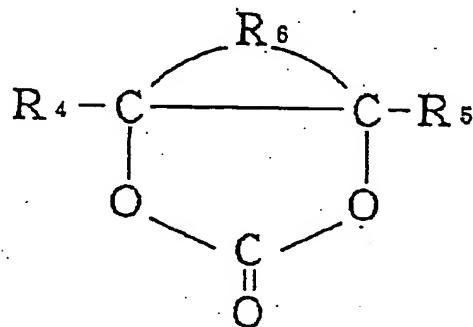
14. An aqueous curable resin composition according to any one of

claims 1 through 6, wherein said 1,3-dioxolan-2-one group is one represented by a general formula [I] below:



(wherein R¹, R² and R³ each may be same or different, and each represents a hydrogen atom or an alkyl group having 1-4 carbon atoms.)

15. An aqueous curable resin composition according to any one of claims 1 through 6, wherein said 1,3-dioxolan-2-one group is one represented by a general formula [II] below:



(wherein R⁴ and R⁵ each may be same or different, and each represents a hydrogen atom or an alkyl group having 1-4 carbon atoms, and

R^6 represents an alkylene group having 3-10 carbon atoms, an alkylene group having 3-10 carbon atoms and having a substituent group such as a halogen atom or an alkoxy group, or an oxy-alkylene group having 3-10 carbon atoms).

[Detailed Description of the Invention]

[0001]

[Field of the Industrial Applicability]

The present invention relates to a novel and useful aqueous curable resin composition. More particularly, it relates to an aqueous curable resin composition which forms curable products with excellent chemical resistance and water resistance, and which contains:

an aqueous dispersion or an aqueous solution of a polymer which contains both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, and an aqueous dispersion or an aqueous solution of a polymer which contains no 1,3-dioxolan-2-one group;

[0002]

an aqueous dispersion or an aqueous solution of a polymer which contains both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, and a curing agent, which is capable of reacting with a hydroxyl group; or

[0003]

an aqueous dispersion or an aqueous solution of a polymer which contains both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, an aqueous dispersion or an aqueous solution of a polymer which contains no 1,3-dioxolan-2-one group, and a curing agent, which is capable of reacting with a hydroxyl group.

[0004]

The composition of the present invention is extremely useful in the fields of paints, adhesives, sealing agents, fiber treating agents and so on.

[0005]

[Prior Arts]

Conventional aqueous curable resin compositions for paints and

adhesives have been prepared by mixing an amino resin, block isocyanate and the like as a curing agent with an aqueous resin. The aqueous resin has been obtained by neutralizing a vinyl polymer, a polyester resin, an alkyd resin, a polyurethane resin and the like which have both of a hydroxyl group and a carboxyl group with a basic substance, and by dispersing or dissolving in water.

[0006]

However, a coated and hardened film of such conventional compositions generally suffers from lack of chemical resistance such as alkali resistance and acid resistance and a lack of water resistance. Therefore, the conventional compositions are of limited use.

[0007]

[Problems to be Solved by the Invention]

The present inventors made an extensive study to overcome the drawbacks of the conventional compositions and to provide an aqueous resin, which is improved in its curing property and in chemical resistance and water resistance.

[0008]

The problems to be solved by the invention are, therefore, to provide an aqueous curable resin composition which forms curable products improved in its curing property and, particularly, in its chemical resistance and water resistance.

[0009]

[Means for solving the Problems]

The present inventors have completed the present invention based on the discovery of a composition which hardens swiftly under heat and results curable products of excellent chemical resistance and water resistance. The discovered composition is a composition composed by mixing:

an aqueous dispersion or an aqueous solution of a polymer which contains both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group with an aqueous dispersion or an aqueous solution of a polymer which contains no 1,3-dioxolan-2-one group;

[0010]

an aqueous dispersion or an aqueous solution of a polymer which contains both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, with a curing agent, which is capable of reacting with a hydroxyl group; or

[0011]

an aqueous dispersion or an aqueous solution of a polymer which contains both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, with an aqueous dispersion or an aqueous solution of a polymer which contains no 1,3-dioxolan-2-one group and with a curing agent, which is capable of reacting with a hydroxyl group.

[0012]

That is, the composition of the present invention contains, as indispensable components,

an aqueous dispersion or an aqueous solution of a polymer (A) which contains, in each molecule, both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, and an aqueous dispersion or an aqueous solution of a polymer (B) which contains no 1,3-dioxolan-2-one group;

[0013]

an aqueous dispersion or an aqueous solution of a polymer (A) which contains, in each molecule, both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, and a curing agent (C) capable of reacting with a hydroxyl group; or

[0014]

an aqueous dispersion or an aqueous solution of a polymer (A) which contains, in each molecule, both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group, an aqueous dispersion or an aqueous solution of a polymer (B) which contains no 1,3-dioxolan-2-one group, and a curing agent (C) which is capable of reacting with a hydroxyl group.

[0015]

The composition may further contain a curing catalyst (D) to form an aqueous-curable resin composition, which is improved in its curing

property, in chemical resistance and in water resistance, and is therefore highly useful.

[0016]

The following provides a detailed explanation of the structure of the present invention.

In the explanation, the polymer (A) which contains both of a carboxyl group and/or a carboxylate group and a 1,3-dioxolan-2-one group means a polymer which contains, in each molecule, at least 0.5, and preferably at least one carboxyl group and/or a carboxylate group ($=\text{COO}^-$) and at least 0.5, and preferably at least one 1,3-dioxolan-2-one group.

[0017]

Typical examples of the polymer (A) are a vinyl polymer, a polyester resin, an alkyd resin, a polyether resin, a polyurethane resin and a polyamide resin. Further examples are a block or graft polymer of the above vinyl polymer and of a polymer other than the vinyl polymer.

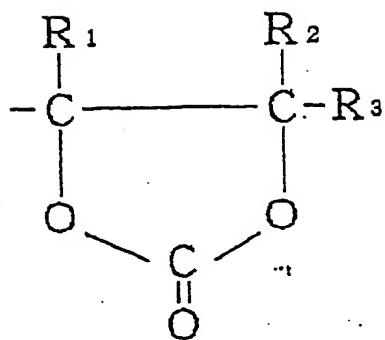
[0018]

Particular representative examples of the vinyl polymer among the above polymers (A) are an acrylic polymer, a vinyl ester polymer, an aromatic vinyl polymer, an α -olefin polymer, a chlorinated olefin polymer and a fluoro olefin polymer.

[0019]

Typical examples of the 1,3-dioxolan-2-one group to be introduced into the polymer (A) are those which are shown by the following general formula [I] or [II]. In the case of 1,3-dioxolan-2-one group having a ring structure as shown by the formula [III], it should be understood that the alkylene group represented by R^6 is bonded to the polymer (A) via a carbon atom of the alkylene group.

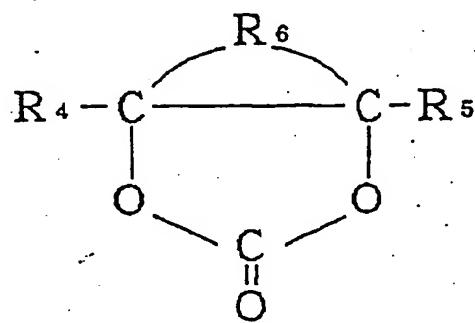
[0020]



[0021]

(wherein R^1 , R^2 and R^3 each may be same or different, and each represents a hydrogen atom or an alkyl group having 1-4 carbon atoms.)

[0022]



[0023]

(wherein R^4 and R^5 each may be same or different, and each represents a hydrogen atom or an alkyl group having 1-4 carbon atoms, and R^6 represents an alkylene group having 3-10 carbon atoms, an alkylene group having 3-10 carbon atoms and having a substituent group such as a halogen atom or an alkoxy group, or an oxy-alkylene group having 3-10 carbon atoms).

Concrete examples of the 1,3-dioxolan-dioxolan-2-one group are 1,3-dioxolan-2-one-dioxolan-2-one-4-yl group, 4-methyl-1,3-dioxolan-2-one-4-yl group, 5-methyl-1,3-dioxolan-2-one-4-yl group, 4,5-dimethyl-1,3-dioxolan-2-one-4-yl group, 4,5,5-trimethyl-1,3-dioxolan-2-one-4-yl group, 4-ethyl-1,3-dioxolan-2-one-4-yl group, 5-ethyl-1,3-dioxolan-2-one-4-yl group, 4-n-propyl-

1,3-dioxolan-2-one-4-yl group, 5-n-propyl-1,3-dioxolan-2-one-4-yl group, 4-n-butyl-1,3-dioxolan-2-one-4-yl group,

[0024]

5-n-butyl-1,3-dioxolan-2-one-4-yl group, 4,5-di-n-butyl-1,3-dioxolan-2-one-4-yl group, 3,4-carbonatecyclohexyl group, 1,2-carbonatecyclohexyl group, 2,3-carbonatecyclohexyl group, 3-methyl-3,4-carbonatecyclohexyl group, 1-methyl-3,4-carbonatecyclohexyl group, 6-methyl-3,4-carbonatecyclohexyl group, 1,2-carbonatecyclopentyl group, 2,3-carbonatecyclopentyl group, 3,4-carbonatecyclopentyl group, 4,5-carbonatecyclooctyl group and 4,5-carbonatecyclododecyl group.

[0025]

Various methods may be used to prepare a vinyl polymer (A) containing both of the 1,3-dioxolan-2-one group and the carboxyl group and/or the carboxylate group. The methods comprise the steps of:

1) copolymerizing a vinyl monomer containing a 1,3-dioxolan-2-one group and a monomer containing a carboxyl group and/or a monomer containing a carboxylate group in the presence, if necessary, of other copolymerizable monomers;

[0026]

2) copolymerizing a vinyl monomer containing a 1,3-dioxolan-2-one group and a monomer containing a carboxyl group in the presence, if necessary, of other copolymerizable monomers, and

neutralizing the carboxyl group introduced into the copolymer, partially or completely, with a basic substance; or

[0027]

3) reacting a vinyl polymer containing a carboxylic anhydride with a compound containing both of a hydroxyl group and 1,3-dioxolan-2-one group. Among these methods, the method shown by the step 2) above is most convenient.

[0028]

Typical examples of the vinyl monomer having 1,3-dioxolan-2-one group used for the method comprising the step 2) are (meth)acrylic acid ester monomers such as 4-(meth)acryloyloxymethyl-1,3-dioxolan-2-one, 4-

methyl-4-(meth)acryloyloxymethyl-1,3-dioxolan-2-one,
4-(meth)acryloyloxymethyl-4,5-dimethyl-1,3-dioxolan-2-one,
4-ethyl-4-(meth)acryloyloxymethyl-1,3-dioxolan-2-one,
4-n-propyl-4-(meth)acryloyloxymethyl-1,3-dioxolan-2-one,
4-n-butyl-4-(meth)acryloyloxymethyl-1,3-dioxolan-2-one,
4-[2-(meth)acryloyloxyethoxymethyl]-1,3-dioxolan-2-one, and
4-methyl-4-[2-(meth)acryloyloxyethoxymethyl]-1,3-dioxolan-2-one;

[0029]

crotonate monomers such as 4-crotonoyloxymethyl-1,3-dioxylane-2-one, 4-methyl-4-crotonoyloxymethyl-1,3-dioxylane-2-one; vinyl ester monomer such as monovinylmono-(1,3-dioxolan-2-one-4ylmethyl)succinate and monovinylmono-1,3-dioxolan-2-one-4ylmethyl)adipate;

[0030]

and vinyl ether monomers such as 4-vinyloxymethyl-1,3-dioxolan-2-one, and 4-methyl-4-vinyloxymethyl-1,3-dioxolan-2-one.

[0031]

Particularly typical examples of the vinyl monomer having a carboxyl group, used for preparing the vinyl polymer, are acrylic acid, methacrylic acid, crotonic acid, monovinyl adipate, monobutyl maleate, monobutyl itaconate, maleic acid, fumaric acid and itaconic acid.

[0032]

Particularly typical examples of the other polymerizable monomer used for preparing the vinyl polymer (A) are:

alkyl(meth)acrylates having 1 to 22 carbon atoms such as methyl(meth)acrylate, ethyl(meth)acrylate, butyl(meth)acrylate, 2-ethylhexyl(meth)acrylate, lauryl(meth)acrylate and stearyl(meth)acrylate;

[0033]

cycloalkyl(meth)acrylates such as cyclopentyl(meth)acrylate, cyclohexyl(meth)acrylate and isobornyl(meth)acrylate; aralkyl(meth)acrylates such as benzyl(meth)acrylate and phenethyl(meth)acrylate;

[0034]

crotonates such as methyl crotonate, ethyl crotonate and n-butyl crotonate;

vinyl carboxylates such as vinyl acetate, vinyl propionate, vinyl benzoate, vinyl pivalate and vinyl varsoate; dialkylesters of unsaturated dibasic acids such as dimethyl maleate, dibutyl maleate, dimethyl fumarate, dibutyl fumarate, dimethyl itaconate and dibutyl itaconate;

[0035]

aromatic vinyl monomers such as styrene, p-tert-butylstyrene, α -methylstyrene and vinyl toluene; alkyl- or cyclohexyl vinylethers such as methylvinyl ether, ethylvinyl ether, isobutylvinyl ether and cyclohexylvinyl ether; α -olefins such as ethylene, propylene and 1-butene; fluoro olefins such as tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene and chlorotrifluoroethylene;

[0036]

monomers having a hydroxyl group such as 2-hydroxyethyl(meth)acrylate, 2-hydroxypropyl(meth)acrylate, 4-hydroxybutyl(meth)acrylate, 2-hydroxyethoxyallyl ether, allyl alcohol, 2-hydroxyethylvinyl ether and 4-hydroxybutylvinyl ether; monomers having carboxylic anhydride groups such as maleic anhydride and itaconic anhydride;

[0037]

monomers having amide groups such as (meth)acrylamide, amide crotonate, N-methylol(meth)acrylamide, N-methylol amide crotonate, N-methylol amide crotonate, N-methoxymethyl(meth)acrylamide, N-butoxymethyl(meth)acrylamide; and monomers having cyano groups such as (meth)acrylonitrile and crotononitrile.

[0038]

Various customary methods may be used to prepare a vinyl polymer containing both of the carboxyl group and the 1,3-dioxolan-2-one group, from the various monomers mentioned above. The most convenient method is to radically polymerize a solution.

[0039]

The polymer (A) can be obtained by a customary radical polymerization process using a known azo or peroxide polymerization initiator with a known solvent such as methanol, ethanol, isopropanol, n-butanol, ethylene glycol monomethyl ether, ethylene glycol monobutyl ether,

cellosolve acetate, acetone, methylethyl ketone, methylisobutyl ketone, toluene and xylene.

[0040]

The carboxyl group introduced into the obtained vinyl polymer containing both of the carboxyl group and the 1,3-dioxolan-2-one group is neutralized with a basic substance of an amount less than equivalent to the carboxyl group, resulting a vinyl polymer containing a carboxyl group, a carboxylate group and a 1,3-dioxolan-2-one group.

[0041]

When the carboxyl group is neutralized with a basic substance in an amount equivalent or more than equivalent to the amount of the carboxyl group, a vinyl polymer containing a carboxylate group and a 1,3-dioxolan-2-one group is obtained.

[0042]

Typical examples of the basic substance used for neutralizing the carboxyl group are alkali metal hydroxides such as sodium hydroxide, potassium hydroxide and lithium hydroxide; carbonates or hydrogencarbonates of alkali metals such as sodium carbonate, potassium carbonate, lithium carbonate, sodium hydrogencarbonate and potassium hydrogencarbonate;

[0043]

quaternary ammonium hydroxides such as tetraethyl ammonium hydroxide, tetra-n-butyl ammonium hydroxide and trimethylbenzyl ammonium hydroxide;

[0044]

and tertiary amines such as trimethyl amine, triethyl amine, tri-n-butyl amine, tri-n-propyl amine, dimethylcyclohexyl amine, dimethylbenzyl amine, dimethylethanol amine, 1-dimethylamino-2-propanol and N-methyl morpholine. Among the basic substances mentioned above, quaternary ammonium hydroxides and tertiary amines are preferable from the point of the chemical resistance, and resistance to water, of the coated films.

[0045]

For preparing the polymer (A) other than the vinyl polymer, such as

a polyester resin, an alkyd resin, a polyether resin and a polyurethane resin which contains both of a 1,3-dioxolan-2-one group and a carboxyl group, it is convenient to react either of the previously prepared resins which contains both of a hydroxyl group and a carboxyl group with a compound containing both of an isocyanate group and a 1,3-dioxolan-2-one group.

[0046]

The carboxyl group of the obtained resin containing both of a 1,3-dioxolan-2-one group and a carboxyl group is then neutralized, partially or completely, with the basic substance mentioned previously, to obtain a polymer (A) containing three groups of a 1,3-dioxolan-2-one group, a carboxyl group and a carboxylate group, or a polymer (A) containing two groups of a 1,3-dioxolan-2-one group and a carboxyl group, respectively.

[0047]

Into the obtained polymer (A), a hydroxyl group is introduced to increase the cross-linking density in the resulted hardened matter. The amount of the 1,3-dioxolan-2-one group introduced into the polymer (A) is preferably 0.15 to 6 mol, and more preferably 0.2 to 5 mol per 1,000 g of the dry weight of the polymer (A).

[0048]

The amount of the carboxyl group and/or the carboxylate group introduced into the polymer (A) is preferably 0.15 to 6 mol, and more preferably 0.2 to 5 mol per 1,000 g of the dry weight of the polymer (A).

[0049]

There are various methods to obtain an aqueous dispersion or an aqueous solution of the polymer (A). They are: 1) to add an organic solvent solution of the polymer (A) to water to make an aqueous dispersion or an aqueous solution and to remove the organic solvent, if necessary;

[0050]

2) to add an organic solvent solution of the polymer (A) to water containing protective colloids and an emulsifier to make an aqueous dispersion or an aqueous solution and to remove the organic solvent, if necessary;

[0051]

3) to add water to an organic solvent solution of the polymer (A) and to remove the solvent, followed by converting the phase to an emulsified phase;

4) to add water containing protective colloids and an emulsifier to an organic solvent solution of the polymer (A) and to remove the solvent, followed by converting the phase to an emulsified phase.

[0052]

For obtaining an organic solvent solution of a vinyl polymer, there are methods in addition to those mentioned above, such as:

5) by emulsion-polymerizing or by solution-polymerizing, in a medium including water, a monomer mixture of a vinyl monomer containing a 1,3-dioxolan-2-one group as an indispensable ingredient and of a monomer containing a carboxyl group and/or a monomer containing a carboxylate group; and

[0053]

6) by emulsion-polymerizing or by solution-polymerizing, in a medium including water, a monomer mixture of a carboxyl group-containing vinyl monomer and of a vinyl monomer containing a 1,3-dioxolan-2-one group as an indispensable ingredient, and by neutralizing the carboxyl group with a basic substance to convert it to a carboxylate group.

[0054]

The polymer (B), which contains no 1,3-dioxolan-2-one group, means one which does not contain any of the 1,3-dioxolan-2-one group. Typical examples of the polymer (B) are a vinyl polymer, a polyester resin, an alkyd resin, a polyether resin, a polyurethane resin and a polyamide resin, and a block- or graft-polymer of the vinyl polymer and of a polymer other than the vinyl polymer.

[0055]

Among the polymers listed above, typical examples of the vinyl polymer are an acrylic polymer, a vinylester polymer, an aromatic vinyl polymer, an α -olefin polymer, a chlorinated olefin polymer and a fluorooolefin polymer.

[0056]

As the polymer (B), a polymer which contains neither of a polar group nor a 1,3-dioxolan-2-one group may be used. The polymer (B) preferably contains at least one group selected from a carboxyl group, a carboxylate group and a hydroxyl group, in view of the curable property and the stability of ingredients.

[0057]

The polar group-containing polymer as the polymer (B) can be prepared by a conventional method. The prepared polymer (B) is treated in a manner the same as that for the polymer (A) to prepare an aqueous dispersion or an aqueous solution.

[0058]

In the case of a vinyl polymer, an aqueous dispersion of the polymer (B) can be prepared directly from at least one vinyl monomer selected from a group consisting of a carboxyl group-containing vinyl monomer, a carboxylate-containing vinyl monomer and a hydroxyl group-containing vinyl monomer, by emulsion-polymerizing or solution-polymerizing the monomer.

[0059]

The amount of the polar group such as the carboxyl group, carboxylate group or hydroxyl group to be introduced into the polymer (B) is 0.05 to 10 mol, preferably 0.1 to 8 mol, per 1,000 g of the dry weight of the polymer (B). When the amount is less than 0.05 mol, the composition of the invention becomes unstable and the curing property becomes insufficient while when the amount exceeds 10 mol, the water resistance and the chemical resistance are lowered.

[0060]

It is possible to improve the curing property by mixing a curing agent (C), which is capable of reacting with a hydroxyl group, into the composition of the invention. Typical examples of the curing agent (C) are various amino resins such as a melamine resin, a urea resin, a benzoguanamine resin and a acetoguanamine resin; and a block isocyanate obtained by blocking any one of various conventionally known polyisocyanates with an active hydrogen-containing compound.

[0061]

The curing catalyst (D) used for the invention means a compound useful for ring-opening the 1,3-dioxolan-2-one group or a compound useful for promoting the reaction of the 1,3-dioxolan-2-one group with the carboxyl group.

[0062]

Particularly typical examples of the catalyst are various kinds of quaternary ammonium salts such as tetramethyl ammonium fluoride, tetrabutyl ammonium fluoride, tetramethyl ammonium chloride, tetramethyl ammonium bromide, tetramethyl ammonium acetate, tetrabutyl ammonium-2,2-dimethyl pentanoate, trimethylbenzyl ammonium -2,2-dimethyl pentanoate, and trimethylbenzyl ammonium propionate;

[0063]

tertiary amines of a strong base such as diazabicyclooctane, diazabicycloundecyne and diazabicyclononene; various kinds of phosphines such as triphenyl phosphine, tri-n-butyl phosphine and tri-n-octyl phosphine; and

[0064]

various kinds of phosphonium salts such as triphenyl benzyl phosphonium fluoride, triphenyl benzyl phosphonium chloride, tri-n-butylbenzyl phosphonium fluoride and tri-n-butylbenzyl phosphonium chloride.

[0065]

To prepare the composition of the invention from the aqueous dispersion or the aqueous solution of the polymer (A) and the aqueous dispersion or the aqueous solution of the polymer(B), the solid content weight ratio of the two components is adjusted as (A) : (B) =2 : 98 to 98 : 2, and more preferably 5 :95 to 95 : 5.

[0066]

To prepare the composition of the invention from the aqueous dispersion or the aqueous solution of the polymer (A) and the curing agent (C), the component (C) is mixed in an amount of 100 weight parts or less, preferably 50 weight parts or less, of the solid content into 100 parts by weight of the solid content of the polymer (A).

[0067]

To prepare the composition of the invention from three components, i.e., the aqueous dispersion or the aqueous solution of the polymer (A), the aqueous dispersion or the aqueous solution of the polymer (B) and the curing agent (C),

the solid content weight ratio of the first two components is adjusted firstly as (A) : (B) = 2 : 98 to 98 : 2, preferably 5 : 95 to 95 : 5. Then, component (C) is mixed into components (A) and (B) in such a ratio that 100 parts by weight or less, preferably 50 parts by weight or less, of the solid content of the component (C) is mixed into 100 parts by weight of the total solid content of components (A) and (B).

[0068]

To prepare the composition of the invention from components including the polymer (A) as an indispensable component with a curing catalyst (D), the components other than the catalyst (D) are firstly adjusted to be in the solid content weight ratio as mentioned above. Then, the component (D) is mixed in a ratio of 60 mmol or less, preferably 40 mmol or less into 100 g of the components other than the catalyst (D).

[0069]

The obtained aqueous curable resin composition of the invention can be used without being colored or it may be colored with a pigment.

[0070]

If necessary, to the aqueous curable resin composition of the present invention may contain various known additives such as a ultraviolet absorbing agent, an oxidation preventing agent, a pigment dispersing agent and a leveling agent as well as a water-soluble organic solvent.

[0071]

The composition of the present invention can be applied to, in various uses and in a wide range, various paints for general coating of a metal, plastic and inorganic substrate, and so on, and for electro-painting. Further, it can also be used for fiber-processing, a sealing agent, an adhesive, and so on.

[0072]

The composition of the present invention is coated onto or impregnated into a base material and is heated at a temperature of 100 to 250°C for 30 seconds to 1 hour, whereby a useful cured product is obtained.

[Examples]

The following provides a detailed explanation the present invention by way of reference examples, working examples and comparative examples. In the following all parts and % are based on weight unless otherwise defined.

[0074]

Reference Example 1

[Preparation of an aqueous substance of a vinyl polymer (A) containing both of a 1,3-dioxolan-2-one group and a carboxylate group]

66 parts of isopropyl alcohol was charged into a reactor equipped with a stirrer, a thermometer, a nitrogen introducing tube, a cooling tube and a dropping funnel, and was heated under nitrogen atmosphere to 80°C. Then, a mixture of 30 parts of methylmethacrylate, 30 parts of n-butylmethacrylate, 12 parts of n-butylacrylate, 20 parts of 4-methacryloyloxyethyl-1,3-dioxolan-2-one, 8 parts of acrylic acid and 2 parts of t-butylperoxy-2-ethylhexanoate was added dropwise thereto over a period of 3 hours. For 10 hours after the dropping, the mixture was maintained at the temperature to obtain a solution of a vinyl polymer having 60 % of nonvolatile content (hereinafter referred to as NV), having a number average molecular weight of 19,000 and having, in each molecule, both of a 1,3-dioxolan-2-one group and a carboxyl group.

[0075]

To the thus obtained solution of the polymer was added 11.2 parts of triethyl amine and 44.2 parts of isopropyl alcohol, and the solution was sufficiently stirred. A solution of a polymer, wherein 100 % of the carboxyl group was neutralized, was obtained, which is hereinafter referred to as A-1.

[0076]

Then, 148.3 parts of water was added to A-1 while being stirred to obtain a homogeneous solution. A part of the isopropyl alcohol was removed from the homogeneous solution under a reduced pressure to obtain an

aqueous resin solution having NV of 40 %, which is referred to as W-I-1.

[0077]

Reference Example 2

[Preparation of an aqueous substance of a vinyl polymer (A) containing a 1,3-dioxolan-2-one group, a carboxyl group, a carboxylate group and a hydroxyl group]

66 parts of isopropyl alcohol was charged into the same reactor as that used in Reference example 1, and was heated under a nitrogen atmosphere to 80°C. Then, a mixture of 30 parts of methylmethacrylate, 10 parts of styrene, 15 parts of n-butylmethacrylate, 10 parts of 2-ethylhexylacrylate, 30 parts of mono(1,3-dioxolan-2-one-4-ylmethyl) ester of itaconic acid, 5 parts of 2-hydroxyethylmethacrylate, 34 parts of isopropyl alcohol and 4 parts of t-butyperoxy-2-ethylexanoate was dropped for 3 hours. For 10 hours after the dropping, the mixture was maintained at the temperature to obtain a solution of a vinyl polymer having NV of 50 %, having a number average molecular weight of 11,000 and having, in one molecule, both of a 1,3-dioxolan-2-one-4 group and a carboxyl group.

[0078]

To the thus obtained solution of the polymer was added with 9.3 parts of dimethyl aminoethanol, and was sufficiently stirred. A solution of a polymer, wherein 80 % of the carboxyl group was neutralized, was obtained and is hereinafter referred to as A-2.

[0079]

Then, 150 parts of water was added to A-2 while being stirred to obtain a homogeneous solution. A part of isopropyl alcohol was removed from the homogeneous solution under a reduced pressure to obtain an aqueous resin solution having NV of 40 % and is referred to as W-I-2.

[0080]

Reference Example 3

[Preparation of an aqueous substance of a vinyl polymer (A) containing a 1,3-dioxolan-2-one group, a carboxyl group and a hydroxyl group]

66 parts of methylethyl ketone was charged into the same reactor as

that used in Reference example 1, and was heated under a nitrogen atmosphere to 80°C. Then, a mixture of 30 parts of ethylmethacrylate, 20 parts of n-butylacrylate, 10 parts of cyclohexylmethacrylate, 20 parts of 4-acryloyloxymethyl-4-methyl-1,3-dioxolan-2-one, 10 parts of methacrylic acid, 10 parts of 4-hydroxybutylacrylate, and 4 parts of t-butylperoxy-2-ethylhexanoate was dropped for 5 hours. For 10 hours after the dropping, the mixture was maintained at the temperature to obtain a solution of a vinyl polymer having NV of 50 %, having a number average molecular weight of 6,000 and having, in one molecule, both of a 1,3-dioxolan-2-one-4 group and a carboxyl group.

[0081]

To the thus obtained solution of the polymer was added 12 parts of triethyl amine, and was sufficiently stirred. A solution of a polymer, wherein 100 % of the carboxyl group was neutralized, was obtained, and is hereinafter referred to as A-3.

[0082]

Then, 150 parts of water was added to A-2 while being stirred to obtain a dispersion. Methyl ethyl ketone was removed from the dispersion under a reduced pressure to obtain an aqueous resin solution having NV of 40 %, and is referred to as W-I-3.

[0083]

Reference Example 4

[Preparation of an aqueous substance of a vinyl polymer (A) containing a 1,3-dioxolan-2-one group and a carboxyl group]

Into a stainless steel autoclave whose atmosphere was sufficiently replaced with nitrogen were charged 50 g of ethylvinyl ether, 72 g of 4-vinyloxymethyl-1,3-dioxolan-2-one, 86 g of monovinyl acetate, 67 g of "Veova 9" (a vinyl ester of a branched aliphatic monocarboxylic acid whose alkyl has 9 carbon atoms, supplied by Shell Co., the Netherlands), 333 g of methyl ethyl ketone and 15 g of 2,2'-azobis(2,4-dimethylvaleronitrile).

[0084]

Then, 225 g of liquefied chlorotrifluoroethylene was forced under pressure thereinto and was stirred. After having been subjected to reaction

for 15 hours at 60°C, unreacted chlorotrifluoroethylene was purged to give a solution of a vinyl polymer having NV of 58%, having a number average molecular weight of 15,000 and having both of a 1,3-dioxolan-2-one group and a carboxyl group.

[0085]

To the thus obtained solution of the polymer was added 51 g of triethyl amine, and was sufficiently stirred. A solution of a polymer, wherein 100 % of the carboxyl group was neutralized, was obtained, and is hereinafter referred to as A-4.

[0086]

Then, 953 g of water was added to A-4 while being stirred to obtain a dispersion. Methylethyl ketone was removed from the dispersion under a reduced pressure to obtain an aqueous resin dispersion having NV of 36 %, and is referred to as W-I-4.

Reference Example 5

[Preparation of an aqueous substance of a polyester resin (A) containing a 1,3-dioxolan-2-one group and a carboxylate group]

Into a reactor equipped with a thermometer, a nitrogen introducing tube, a fractionating tube and a stirrer were charged 287.6 parts of hexahydrophthalic anhydride, 117 parts of adipic acid, 59.2 parts of neopentylglycol, and 190 parts of trimethylol propane and elevated the temperature gradually from 150°C to 190°C for a period of 2 hours. The temperature was maintained for 4 hours to continue the reaction and was lowered. 400 parts of methylethyl ketone was added to the resultant to obtain 1,011 parts of a solution of polyester resin intermediate which has an acid value of 105 and a hydroxyl value of 100 of the solid content.

[0087]

After the fractionating tube was replaced by a reflux condenser, 254 parts of isophorone diisocyanate, 135 parts of 4-hydroxymethyl-1,3-dioxolan-2-one and 0.05 parts of dibutyltin dilaurate were added to proceed an addition reaction for 5 hours at 78°C.

[0088]

After 398 parts of dipropylene glycol monomethyl ether was added

to the resultant, 370 parts of methylethyl ketone was removed under a reduced pressure to obtain a polyester solution having NV of 70 %, an acid value of the solid content of 61.0 and having both of a 1,3-dioxolan-2-one group and a carboxyl group.

[0089]

To the thus obtained polyester solution was added 110 parts of triethyl amine so that 100 % of the carboxyl group may be neutralized. A polyester resin solution having both of a 1,3-dioxolan-2-one group and a carboxyl group was obtained, and is hereinafter referred to as A-5.

[0090]

Then, 928 parts of water was added to the polyester resin solution (A-5) while being well stirred to obtain an aqueous resin solution having NV of 36 %, and having both of a 1,3-dioxolan-2-one group and a carboxylate group, and is referred to as W-I-5.

[0091]

Reference Example 6

[Preparation of an aqueous substance of a polyether resin (A) containing a 1,3-dioxolan-2-one group, a carboxyl group and a carboxylate group]

Into the same reactor as that of Reference example 1 were charged 2,000 parts of polypropylene glycol having a molecular weight of 2,000, 1,000 parts of methylethyl ketone, 286 parts of an adduct of 4-hydroxymethyl-1,3-dioxolan-2-one and hexamethylene diisocyanate in a molar ratio of 1:1, and 0.05 parts of dibutyltindilaurate. The resultant mixture was heated to 78°C and subjected to an addition reaction for 5 hours.

[0092]

Then, 100 parts of succinic anhydride and 10 parts of triphenylphosphine were added to the mixture at the same temperature, and the mixture was subjected to reaction for 10 hours to give a solution of a polyether having both of a 1,3-dioxolan-2-one group and a carboxylate group.

[0093]

To the thus obtained polyester solution was added 50.5 parts of triethyl amine so that 50% of the carboxyl group may be neutralized. A polyether resin solution having a 1,3-dioxolan-2-one group, a carboxyl group and a carboxylate group was obtained, and is hereinafter referred to as A-6.

[0094]

Then, the resin solution (A-6) was added to 2,000 parts of water while being stirred. Methylethyl ketone was distilled away under a reduced pressure, to obtain an aqueous resin solution having NV of 54.9% and having a carboxyl group, a carboxylate group and a 1,3-dioxolan-2-one group, and is referred to as W-I-6.

[0095]

Reference Example 7

[Preparation of an aqueous substance of a polyether resin (A) containing a 1,3-dioxolan-2-one group, a carboxyl group and a carboxylate group]

Into the same reactor as in Reference example 1 were charged 1,080 parts of an adduct of 2,2-diethylpropylene glycol and ϵ -caprolactone in a mole ratio of 1:2, 672 parts of hexamethylene diisocyanate, 268 parts of dimethylolpropionic acid, 3,411 parts of methyl ethyl ketone and 2 parts of dibutyltindilaurate. The resultant mixture was heated to 80°C under a nitrogen atmosphere and subjected to reaction at the same temperature for 15 hours to give a solution of a polyurethane resin having a hydroxyl group at the both ends.

[0096]

286 parts of an adduct of 4-hydroxymethyl-1,3-dioxolan-2-one and hexamethylene isocyanate in a molar ratio of 1:1 and 0.5 parts of dibutyltindilaurate were added to the solution and were subjected to an addition reaction at 78°C for 5 hours.

[0097]

Then, 100 parts of succinic anhydride and 10 parts of triphenylphosphine were added to the resultant at the same temperature, and the mixture was subjected to reaction for 10 hours to give a solution of a polyurethane having both of a 1,3-dioxolan-2-one group and a carboxylate

group.

[0098]

To the thus obtained resin solution was added 50.5 parts of triethyl amine so that 50% of the carboxyl group may be neutralized. A polyurethane resin solution having a 1,3-dioxolan-2-one group, a carboxyl group and a carboxylate group was obtained, and is hereinafter referred to as A-7.

[0099]

Then, the resin solution (A-7) was added to 2,000 parts of water while being stirred. Methyleneethyl ketone was distilled away under a reduced pressure, to obtain an aqueous resin solution having NV of 55.1% and having a carboxyl group, a carboxylate group and a 1,3-dioxolan-2-one group, and is referred to as W-I-7.

[0100]

Reference Example 8

[Preparation of an aqueous substance of a carboxyl group containing polymer (B)]

Into the same reactor as in Reference example 1, 300 parts of deionized water was charged, and it was heated to 85°C in a nitrogen atmosphere. Thereinto were dropwise added over a period of 2 hours an emulsion obtained by adding 30 parts of methyl methacrylate, 40 parts of n-butyl methacrylate, 20 parts of n-butyl acrylate and 10 parts of methacrylic acid to a solution of 2.5 parts of sodium dodecylbenzenesulfonate in 50 parts of deionized water, and a solution obtained by dissolving 1 part of ammonium persulfate in 50 parts of deionized water.

[0101]

Successively after completion of the dropwise addition, the mixture was held at the same temperature for one hour to complete polymerization, and thereby an aqueous dispersion (emulsion) of a carboxyl group containing polymer (B), containing NV of 20.0% was obtained, and is hereinafter abbreviated as aqueous resin (W-II-1).

[0102]

Reference Example 9

[Preparation of an aqueous substance of a polymer (B) containing a carboxyl group and an hydroxyl group]

An aqueous dispersion of a polymer (B) containing a carboxyl group and an hydroxyl group and having NV of 20.0 % was obtained in the same manner as in Reference example 8 except that 40 parts of methyl methacrylate, 15 parts of n-butylmethacrylate, 5 parts of 2-hydroxyethyl methacrylate and 10 parts of methacrylic acid were used as polymerizable monomers. Hereinafter, it is referred to as aqueous resin (W-II-2).

[0103]

Reference Example 10

[Preparation of an aqueous substance of a polymer (B) containing a carboxylate group and a hydroxyl group]

66 parts of isopropyl alcohol was charged in the same reactor as in Reference example 1 and heated to 80°C under a nitrogen atmosphere.

[0104]

Then, a mixture was dropwise added over a period of 3 hours comprising 10 parts of styrene, 20 parts of methyl methacrylate, 20 parts of n-butyl methacrylate, 15 parts of 2-hydroxyethyl methacrylate, 20 parts of n-butyl acrylate, 15 parts of acrylic acid and 4 parts of tert-butyl peroxy-2-ethylhexanoate.

[0105]

Successively after completion of the dropwise addition, the mixture was held at the same temperature for 10 hours to give a solution, containing NV of 60.0 %, of a carboxyl group-containing acrylic polymer (B-1) having a number average molecular weight (hereinafter referred to as Mn) of 14,000.

[0106]

To the thus obtained polymer solution, 21 parts of triethylamine and 100 parts of the isopropyl alcohol were added and the mixture was sufficiently stirred to give a solution of the polymer whose carboxyl group were neutralized by 100% to a carboxylate group.

[0107]

Then, 150 parts of deionized water was added to this solution with stirring to give a homogeneous solution. Thereafter, a part of the isopropyl

alcohol and water was distilled away from this solution under reduced pressure to give a water-isopropyl alcohol solution of an acrylic polymer containing a carboxylate group, containing NV of 40 %. Hereinafter, this is abbreviated as aqueous resin (W-II-3).

[0108]

Reference Example 11

[Preparation of an aqueous substance of a polymer (B) containing a carboxyl group and a carboxylate group]

To 170 parts of the polymer solution (B-1) obtained by Reference example 10, 7 parts of triethylamine and 100 parts of isopropyl alcohol were added and the mixture was sufficiently stirred to give a solution of the polymer whose carboxyl group were neutralized by 33 % to a carboxylate group.

[0109]

Then, 150 parts of deionized water was added to this solution with stirring to give a uniform solution. Thereafter, all of the isopropyl alcohol and a part of water were distilled away from this solution under reduced pressure to give an aqueous dispersion of a n acrylic polymer, containing NV of 40 % and containing a carboxyl group and a carboxylate group.

Hereinafter, this is abbreviated as aqueous resin (W-II-4).

[0110]

Reference Example 12

(Same as above)

In an one-liter autoclave made of stainless steel whose atmosphere had sufficiently been replaced with nitrogen were charged 70 g of ethylvinyl ether, 86 g of monovinyl adipate, 119 g of "Veober 9", 333 g of methylethyl ketone and 15 g of 2,2'-azobis (2,4-dimethylvaleronitrile). Then, 225 g of liquefied chlorotrifluoroethylene was charged, and the mixture was heated for 15 hours with stirring. Then, unreacted chlorotrifluoroethylene was purged to give a solution, containing NV of 57%, of a carboxyl group-containing fluoroolefin polymer having Mn of 14,000.

[0111]

Then, 22.3g dimethylaminoethanol was added and the resultant

mixture was sufficiently stirred to give a solution of the polymer whose carboxyl group was neutralized by 50%.

[0112]

Thereafter, the whole quantity of this polymer solution was added to a mixture comprising 800 g of deionized water and 50 g of ethyleneglycol monomethyl ether with sufficient stirring to give a dispersion. Then, methylethyl ketone was distilled away under reduced pressure to give an aqueous dispersion of a fluoroolefin polymer, containing NV of 38.1% and containing a carboxyl group and a carboxylate group. Hereinafter, this is abbreviated as aqueous resin (W-II-5).

[0113]

Reference Example 13

(Same as above)

In the same reactor as in Reference example 11 were charged 1,134 parts of an adduct of 2,2-diethylpropylene glycol and ϵ -caprolactone in a mole ratio of 1:2, 672 parts of hexamethylene diisocyanate, 268 parts of dimethylolpropionic acid, 3,411 parts of methylethyl ketone and 2 parts of dibutyltindilaurate. The resultant mixture was heated to 80°C under a nitrogen atmosphere and subjected to reaction at the same temperature for 15 hours to give a solution of a polyurethane resin having a hydroxyl group at both ends.

[0114]

Then, 200 parts of succinic anhydride and 10 parts of diazabicyclooctane were added to this solution at the same temperature, and the mixture was subjected to reaction for 10 hours. After the temperature was lowered, 101 parts of triethyl amine was added so that 50% of the carboxyl group may be neutralized and the mixture was sufficiently stirred. It was obtained a solution of the polymer (B) having a carboxyl group and a carboxylate group.

[0115]

Thereafter, 3,026 parts of deionized water was added to the resin solution with sufficient stirring to give a dispersion, and then, methylethyl ketone was distilled away under reduced pressure to give an aqueous

dispersion of a polyurethane resin, containing NV of 45 %. Hereinafter, this is abbreviated as aqueous resin (W-II-6).

[0116]

Reference Example 14

[Preparation of an aqueous substance of a polymer (B) containing a carboxyl group and a carboxylate group]

In the same reactor as in Reference example 11 were charged 148.7 parts of isophthalic acid, 11.0 parts of trimethylolpropane, 211.7 parts of neopentyl glycol and 66.0 parts of p-tert-butyl benzoic acid. The resultant mixture was heated to 170°C. After it reached the temperature, it was gradually elevated to 220°C for a period of four hours.

[0117]

The mixture was maintained at 220°C for one hour to continue a reaction and was cooled to 180°C. Then, 65.5 parts of adipic acid, 138.0 parts of hexahydrophthalic anhydride and 13.2 parts of maleic anhydride were added thereto and the mixture was maintained at 155°C for one hour and, then, heated gradually to 220°C for a period of 4 hours.

[0118]

After the mixture was subjected to reaction for 3 hours, the fractionating tube was replaced with a reflux cooling pipe. While the mixture was gradually cooled, 574 parts of methylethyl ketone was added thereto to give 1,174 parts of a polyester resin solution having an acid value of 70 and a hydroxyl value of 3.

[0119]

To the solution was dropwise added a mixture of 180 parts of styrene, 100 parts of n-butyl methacrylate, 50 parts of n-butyl acrylate, 50 parts of 2-hydroxyethyl methacrylate, 20 parts of acrylic acid and 20 parts of tert-butylperoxyoctoate at 80°C for a period of 4 hours. Successively after completion of the dropwise addition, the mixture was held at the same temperature for 12 hours to be subjected to reaction. As a result, it was obtained a solution of a graft polymer of a polyester resin component containing a carboxyl group and a hydroxyl group and of an acrylic resin

component with a weight ratio of 60/40, which contains NV of 64.0 %, and has an acid value of 57.6 and a hydroxyl value of 23.4 of the solid content of the solution.

[0120]

To this graft polymer solution was added 104 parts of triethyl amine so that 100% of the carboxyl group may be neutralized, with sufficient stirring. It was obtained a solution of a graft polymer, containing both of a carboxyl group and a hydroxyl group.

[0121]

To the whole quantity of this polymer solution was added 1.654 parts of deionized water with sufficient stirring to give a dispersion. Then, methylethyl ketone was distilled away under reduced pressure to give an aqueous dispersion of a graft polymer of polyester resin-acrylic resin, containing NV of 40%. Hereinafter, this is abbreviated as aqueous resin (W-II-7).

[0122]

Reference Example 15

[Preparation of a curing agent capable of reacting with a hydroxyl group]

In the same reactor as in Reference example 1 were charged 1,000 parts of "Burnock DN-980S" [an aliphatic polyisocyanate resin produced by DAINIPPON INK AND CHEMICALS, INC.; NV content=100%, NCO content=20%], 331 parts of methylethyl ketoxime, 1.4 parts of dibutyltindilaurate and 1.473 parts of methylethyl ketone, and the resultant mixture was heated to 80°C in a nitrogen atmosphere and then held at the same temperature for 10 hours.

[0123]

Then, 142 parts of 2-hydroxymethyl-2-methoxymethylpropionic acid was added, and the mixture was subjected to reaction for 10 hours to give a solution, containing NV of 50%, of a carboxyl group-containing blocked isocyanate resin.

[0124]

Thereafter, for the purpose of neutralizing 100% of the thus

introduced carboxyl group, 96.9 parts of triethylamine was added, followed by sufficient stirring. Then, 1,570 parts of deionized water was added to the thus obtained solution with sufficient stirring to give a dispersion.

[0125]

Further, methylethyl ketone was distilled away from this dispersion under reduced pressure to give an aqueous dispersion of a blocked isocyanate resin, containing NV of 50%. Hereinafter, this is abbreviated as curing agent (C-1).

[0126]

Working Examples 1 to 11 and Comparative Examples 1 and 2

Various components were compounded in the ratio shown in Table 1 to obtain compositions for clear coatings.

[0127]

Then, the thus obtained respective compositions were applied, using an applicator, onto zinc phosphate-treated steel plates having 0.8 mm thickness to give coats of 30 μ m dry thickness, which were baked under the prescribed condition to give cured films.

[0128]

The obtained respective cured films were evaluated for chemical resistance, water resistance and gelling ratio, and the results were shown in Table 1.

[0129]

Table 1 (1-1)

Mixing Ratio	Aqueous Material of Polymer (A)	Examples		
		1	2	3
		W-I-1	100	
		W-I-2		100
		W-I-3		100
		W-I-4		
		W-I-5		
	Aqueous Material of Polymer (A)	W-I-6		
		W-I-7		
		W-II-1		50
		W-II-2		
		W-II-3		
		W-II-4		
		W-II-5		
	Curing Agent (C)	W-II-6		
		W-II-7		
	Curing Agent (C)	C-1	30	
		S-695		6.7
	Curing Catalyst (D)	TMBAHO		
		TBAF		
		TBAA		0.5

[0130]

Table 1 (1-2)

Curing Condition (° C/min.)	Curing Property (gelling ratio; %)	Examples		
		1	2	3
		160/30	1/	140/20
Coated Film Performance	Water Resistance		No problem	
	Acid Resistance		No problem	
	Alkali Resistance		No problem	

[0131]

Note:

TMBAHO...trimethylbenzyl ammonium hydroxide

TBAF...tetra-n-butyl ammonium fluoride

TBAA...tetra-n-butylammonium acetate

S-695 "Watersol S-695" [methyl-etherified methylolmelamine produced by DAINIPPON INK AND CHEMICALS, INC.; solvent=water, nonvolatile matters=66%].

[0132]

"curing property" is the value obtained such that each of peeled off coated films was immersed in acetone at room temperature over a period of 24 hours, that the remaining undissolved film was dried at 110°C for one hour, that the weight of the obtained dried film was divided by the weight of the film prior to being immersed, and that the obtained quotient was multiplied by 100.

"Water resistance" was evaluated by immersing each cured film in 60°C water for 7 days and then judging the state of the coated surface of the film by visual observation.

"Acid resistance" was evaluated by immersing each cured film in 10% H_2SO_4 aqueous solution at 30°C for 24 hours and then judging changes in the state of the coat surface by visual observation.

"Alkali resistance" was evaluated by immersing each cured film in 10% $NaOH$ aqueous solution at 30°C for 24 hours and then judging changes in the state of the coat surface by visual observation.

[0133]

Table 1 (2-1)

Mixing Ratio	Aqueous Material of Polymer (A)	Examples		
		4	5	6
	W-I-1			
	W-I-2			
	W-I-3	100		
	W-I-4		100	
	W-I-5			100
	Aqueous Material of Polymer (A)	W-II-1		50
		W-II-2		
		W-II-3		
		W-II-4		
		W-II-5	23	
		W-II-6		100
		W-II-7		
	Curing Agent (C)	C-1	30	20
		S-695	6.7	
	Curing Catalyst (D)	TMBAHO		1
		TBAF		
		TBAA		

[0134]

Table 1 (2-2)

Coated Film Performance		Examples		
		4	5	6
		160/30		140/20
Curing Condition (° C/min.)				
Curing Property (gelling ratio; %)		94.1	94.9	93.0
Coated Film Performance	Water Resistance	No problem		Slight lowering of gloss
	Acid Resistance	No problem		Same as above
	Alkali Resistance	No problem		Same as above

[0135]

Table 1 (3-1)

Mixing Ratio	Aqueous Material of Polymer (A)	Examples		
		7	8	9
		W-I-1		
		W-I-2		
		W-I-3		
		W-I-4		
		W-I-5		100
	Aqueous Material of Polymer (A)	W-I-6		
	W-I-7	100		
	W-II-1			
	W-II-2			
	W-II-3			
	W-II-4			
	W-II-5			
	W-II-6			
	W-II-7			
	Curing Agent (C)	C-1	15	30
	S-695			
	Curing Catalyst (D)	TMBAHO		
	TBAF			
	TBAA	0.6		

[0136]

Table 1 (3-2)

Curing Condition (° C/min.)	Examples		
	7	8	9
	140/20		160/30
Curing Property (gelling ratio; %)	93.5	95.1	93.0
	Water Resistance	No problem	
	Acid Resistance	No problem	
Coated Film Performance	Alkali Resistance	No problem	

[0137]

Table 1 (4-1)

		Examples	
		10	11
Mixing Ratio	Aqueous Material of Polymer (A)	W-I-1 W-I-2 W-I-3 W-I-4 W-I-5 W-I-6 W-I-7	100 100
	Aqueous Material of Polymer (A)	W-II-1 W-II-2 W-II-3 W-II-4 W-II-5 W-II-6 W-II-7	15 20
	Curing Agent (C)	C-1	40
		S-695	
	Curing Catalyst (D)	TMBAHO	0.5
		TBAF	
		TBAA	

[0138]

Table 1 (4-2)

		Examples	
		10	11
Curing Condition (° C/min.)		140/20	160/20
Curing Property (gelling ratio; %)		94.1	96.0
Coated Film Performance	Water Resistance	No problem	
	Acid Resistance	No problem	
	Alkali Resistance	No problem	

[0139]

Table 1 (5-1)

		Comparative Examples	
		1	2
	Aqueous Material of Polymer (A)	W-I-1 W-I-2 W-I-3 W-I-4 W-I-5 W-I-6 W-I-7	
Mixing Ratio	Aqueous Material of Polymer (A)	W-II-1 W-II-2 W-II-3 W-II-4 W-II-5 W-II-6 W-II-7	100 100
	Curing Agent (C)	C-1 S-695	31 15
	Curing Catalyst (D)	TMBAHO TBAF TBAA	

[0140]

Table 1 (5-2)

		Comparative Examples	
		1	2
Curing Condition (° C/min.)		160/30	
Curing Property (gelling ratio; %)		92.1	92.5
Coated Film Performance	Water Resistance	Blistered all over	
	Acid Resistance	Whitened	
	Alkali Resistance	Whitened	

[0141]

[Technical effect of the invention]

The aqueous curable resin composition of this invention gives cured products excellent especially in chemical resistance and water resistance and, therefore, it has a large merit that it can effectively be utilized in uses such as coatings, adhesives, sealing and fiber treating agents.

[AMENDMENT]

[Filed date] December 24, 1991

[Amendment 1]

[Document to be amended] Specification

[Identifier to be amended] 0024

[Way of amendment] Replacement

[Amended content]

[0024]

5-n-butyl-1,3-dioxolan-2-one-4-yl group, 4,5-di-n-butyl-1,3-dioxolan-2-one-4-yl group, 3,4-carbonatecyclohexyl group, 2,3-carbonatecyclohexyl group, 2,3-carbonatecyclohexyl group, 3-methyl-3,4-carbonatecyclohexyl group, 1-methyl-3,4-carbonatecyclohexyl group, 6-methyl-3,4-carbonatecyclohexyl group, 2,3-carbonatecyclopentyl group, 3,4-carbonatecyclopentyl group, 4,5-carbonatecyclooctyl group and 4,5-carbonatecyclododecyl group.

[Amendment 2]

[Document to be amended] Specification

[Identifier to be amended] 0029

[Way of amendment] Replacement

[Amended content]

[0029]

various crotonate monomers such as 4-crotonoyloxymethyl-1,3-dioxylane-2-one, 4-methyl-4-crotonoyloxymethyl-1,3-dioxylane-2-one; various vinyl ester monomer such as monovinylmono-(1,3-dioxolan-2-one-4ylmethyl)succinate and monovinylmono-1,3-dioxolan-2-one-4ylmethyl)adipate;

[Amendment 3]

[Document to be amended] Specification

[Identifier to be amended] 0066

[Way of amendment] Replacement

[Amended content]

[0066]

To prepare the composition of the invention from the aqueous dispersion or the aqueous solution of the polymer (A) and the curing agent (C), the component (C) is mixed in an amount of 3 to 100 weight parts or less, preferably 5 to 50 weight parts or less of the solid content into 100 parts by weight of the solid content of the polymer (A).

[Amendment 4]

[Document to be amended] Specification

[Identifier to be amended] 0077

[Way of amendment] Replacement

[Amended content]

[0077]

Reference Example 2

[Preparation of an aqueous substance of a vinyl polymer (A) having a 1,3-dioxolan-2-one group, a carboxyl group, a carboxyl ate group and a hydroxyl group]

66 parts of isopropyl alcohol was charged into a reactor same as that used in Reference example 1, and was heated under a nitrogen atmosphere to 80°C. Then, a mixture of 30 parts of methylmethacrylate, 10 parts of styrene, 15 parts of n-butylmethacrylate, 10 parts of 2-ethylhexylacrylate, 30 parts of mono(1,3-dioxolan-2-one-4-ylmethyl) ester of itaconic acid, 5 parts of 2-hydroxyethylmethacrylate, 34 parts of isopropyl alcohol and 4 parts of t-butylperoxy-2-ethylexanoate was dropped for 3 hours. For 10 hours after the dropping, the mixture was maintained at the temperature to obtain a solution of a vinyl polymer having NV of 50%, having a number average molecular weight of 11,000 and having, in one molecule, both of 1,3-dioxolan-2-one-4 groups and a carboxyl group.

[Amendment 5]

[Document to be amended] Specification

[Identifier to be amended] 0129

[Way of amendment] Replacement

[Amended content]

[0129]

Table 1 (1-1)

Mixing Ratio	Aqueous Material of Polymer (A)	W-I-1	100	Examples	
		W-I-2		1	2
		W-I-3			3
		W-I-4			
		W-I-5			
		W-I-6			
		W-I-7			
	Aqueous Material of Polymer (B)	W-II-1			50
	W-II-2				
	W-II-3				
	W-II-4				
	W-II-5				
	W-II-6				
	W-II-7				
	Curing Agent (C)	C-1	30		
	S-695		6.7		
	Curing Catalyst (D)	TMBAHO			0.5
	TBAF				
	TBAA				

[Amendment 6]

[Document to be amended] Specification

[Identifier to be amended] 0130

[Way of amendment] Replacement

[Amended content]

[0130]

Table 1 (1-2)

		Examples		
		1	2	3
Curing Condition (° C/min.)		160/30		140/30
Curing Property (gelling ratio; %)		95.0	94.5	93.4
Coated Film Performance	Water Resistance		No problem	
	Acid Resistance		No problem	
	Alkali Resistance		No problem	

[Amendment 7]

[Document to be amended] Specification

[Identifier to be amended] 0133

[Way of amendment] Replacement

[Amended content]

[0133]

Table 1 (2-1)

Mixing Ratio	Aqueous Material of Polymer (A)	W-I-1 W-I-2 W-I-3 W-I-4 W-I-5 W-I-6 W-I-7	Examples		
			4	5	6
		100		100	100
	Aqueous Material of Polymer (B)	W-II-1 W-II-2 W-II-3 W-II-4 W-II-5 W-II-6 W-II-7			
		23			100
	Curing Agent (C)	C-1 S-695		30	20
	Curing Catalyst (D)	TMBAHO TBAF TBAA			1

[Amendment 8]

[Document to be amended] Specification

[Identifier to be amended] 0134

[Way of amendment] Replacement

[Amended content]

[0134]

Table 1 (2-2)

		Examples		
		4	5	6
Curing Condition (° C/min.)		160/30		140/30
Curing Property (gelling ratio; %)		94.1	94.9	93.0
Coated Film Performance	Water Resistance	No problem		Slight lowering of gloss
	Acid Resistance	No problem		No problem
	Alkali Resistance	No problem		No problem

[Amendment 9]

[Document to be amended] Specification

[Identifier to be amended] 0135

[Way of amendment] Replacement

[Amended content]

[0135]

Table 1 (3-1)

Mixing Ratio	Aqueous Material of Polymer (A)	W-I-1 W-I-2 W-I-3 W-I-4 W-I-5 W-I-6 W-I-7	Examples		
			7	8	9
	Aqueous Material of Polymer (B)	W-II-1 W-II-2 W-II-3 W-II-4 W-II-5 W-II-6 W-II-7		100	100
	Curing Agent (C)	C-1 S-695	15	30	
	Curing Catalyst (D)	TMBAHO TBAF TBAA		0.6	

[Amendment 10]

[Document to be amended] Specification

[Identifier to be amended] 0136

[Way of amendment] Replacement

[Amended content]

[0136]

Table 1 (3-2)

		Examples		
		7	8	9
Curing Condition (° C/min.)		140/30	160/30	
Curing Property (gelling ratio; %)		93.5	95.1	93.0
Coated Film Performance	Water Resistance		No problem	
	Acid Resistance		No problem	
	Alkali Resistance		No problem	

[Amendment 11]

[Document to be amended] Specification

[Identifier to be amended] 0137

[Way of amendment] Replacement

[Amended content]

[0137]

Table 1 (4-1)

Mixing Ratio	Aqueous Material of Polymer (A)	W-I-1 W-I-2 W-I-3 W-I-4 W-I-5 W-I-6 W-I-7	Examples	
			10	11
	Aqueous Material of Polymer (B)	W-II-1 W-II-2 W-II-3 W-II-4 W-II-5 W-II-6 W-II-7		
	Curing Agent (C)	C-1 S-695	15	
	Curing Catalyst (D)	TMBAHO TBAF TBAA	0.5	

[Amendment 12]

[Document to be amended] Specification

[Identifier to be amended] 0138

[Way of amendment] Replacement

[Amended content]

[0138]

Table 1 (3-2)

	Examples	
	10	11
Curing Condition (° C/min.)	140/30	160/30
Curing Property (gelling ratio; %)	9425	96.0
Coated Film Performance	Water Resistance	No problem
	Acid Resistance	No problem
	Alkali Resistance	No problem